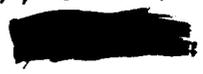


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ALGEBRAIC DESCRIPTION OF ATOM-MOLECULE INTERACTIONS

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Abstract

We describe a new method based on algebraic techniques, which leads to a model of atom-diatom collisions.

1 Introduction

One-dimensional atom-molecule collisions have been studied using a combination of differential and algebraic techniques in conjunction with time evolution operator methods for a variety of molecular potentials [1]. For three-dimensional systems, however, one needs to resort to a number of computational integro-differential techniques to describe such interactions [2,3]. In recent papers we have proposed an algebraic framework based on the vibron model [4], that leads to a three-dimensional scheme for such interactions [5], which starts from a $U(4) \times U(4)$ description of three-atomic molecules. We then apply a coherent state method to one of the $U(4)$'s, thus extracting a coordinate dependence for the interaction between one of the atoms and the remaining diatom, while the latter is still described algebraically. The resulting Hamiltonian is formally analogous to the ones used in one dimension [1] and can be solved in principle in the interaction picture [5]. This is a difficult task, however, particularly with respect to assessing the different degrees of approximation involved. For this reason we consider here a one-dimensional version of our model based on a $U(2) \times U(2)$ dynamical algebra, which is simpler to analyze and already incorporates much of the complexity of the full three-dimensional model.

2 One-Dimensional Model

In our one dimensional model, the stretching vibrations of triatomic molecules are described in terms of the dynamical algebra

$$U_1(2) \times U_2(2) \tag{1}$$

by means of the Hamiltonian

$$\hat{H} = E_0(N_1, N_2) + AJ_{z_1}^2 + BJ_{z_2}^2 + C\hat{J}_{z_1}\hat{J}_{z_2} + D\hat{J}_1 \cdot \hat{J}_2 + \dots, \quad (2)$$

where \hat{J}_{x_i} , \hat{J}_{y_i} , and \hat{J}_{z_i} are the $SU_i(2)$ generators and \hat{N}_i the (fixed) total boson number associated to $U_i(2)$. The dots at the end of (2) indicate that we may also need other combinations of generators, such as $\hat{J}_{y_1} \cdot \hat{J}_{y_2}$. Such Hamiltonians are well suited to describe stretching vibrations, due to the connection that can be established between the $U(2)$ algebra and the one-dimensional Morse oscillator Schrödinger equation [6]. We now introduce the coherent state basis associated to bond number 2 [7],

$$|[N]r\rangle = \frac{1}{\sqrt{N!(1+r^2)^N}} (s^\dagger + rt^\dagger)^N |0\rangle, \quad (3)$$

where s^\dagger , t^\dagger are two scalar boson creation operators through which the $U(2)$ algebras are realized [6]. Computing the expectation value of (2) in the basis (3) and carrying out the coordinate transformation

$$r = \sqrt{\frac{e^{-bx/a_0}}{2 - e^{-bx/a_0}}}, \quad (4)$$

we arrive at a Hamiltonian of the form

$$H = \hat{H}_0 + \hat{V}_1 + \hat{V}_2 + \hat{V}_3, \quad (5)$$

where

$$\hat{H}_0 = AJ_{z_1}^2, \quad (6a)$$

$$\hat{V}_1 = -\hat{\alpha}e^{-bx/2a_0}(2 - e^{-bx/a_0})^{1/2}, \quad (6b)$$

$$\hat{V}_2 = -\beta(2e^{-bx/a_0} - e^{-2bx/a_0}), \quad (6c)$$

$$\hat{V}_3 = \hat{\gamma}e^{-bx/a_0}, \quad (6d)$$

and

$$\hat{\alpha} = -\frac{1}{2}(C + D)N\hat{J}_{z_1}, \quad (7a)$$

$$\beta = -\frac{1}{4}BN(N - 1), \quad (7b)$$

$$\hat{\gamma} = -\frac{1}{2}DN\hat{J}_{y_1}. \quad (7c)$$

The potentials (6b) and (6c) generalize the typical interactions of exponential form (6d) used in previous works [1]. For collision energies high compared with the vibrational excitations, we may “freeze” the molecular coordinates and substitute \hat{J}_{z_1} and \hat{J}_{y_1} in (7a) and (7c) by their

expectation values in the $|jm\rangle$ basis, leading to a well defined potential for which we evaluate classical trajectories, associated to a classical Lagrangian of the form

$$L = \frac{\mu}{2} \dot{x}^2 + V_1(x) + V_2(x) + V_3(x) . \quad (8)$$

Substituting these trajectories $x(t)$ back into (5) then leads to a time-dependent potential of the form

$$\hat{V}(t) = V_1(t)\hat{J}_{x_1} + V_2(t) + V_3(t)\hat{J}_{y_1} + V_4(t)\hat{J}_{x_1} , \quad (9)$$

where $V_i(t)$ are obtained from (6), except for $V_4(t)$, which is identically zero.

We now use the interaction scheme, which is appropriate to determine time-dependent solutions for Hamiltonians of the form $\hat{H} = \hat{H}_0 + \hat{V}(t)$, as in (5). The evolution operator in this scheme satisfies the equation

$$i\hbar \frac{\partial \hat{U}(t)}{\partial t} = \hat{V}_{int} \hat{U}(t) , \quad (10)$$

where

$$\hat{V}_{int}(t) = e^{i\hbar \hat{H}_0(t-t_1)} \hat{V}(t) e^{-i\hbar \hat{H}_0(t-t_1)} . \quad (11)$$

A great simplification arises when \hat{V}_{int} is a linear combination of a closed algebra. For the particular case of $SU(2)$, $U(t_1, t)$ can be expressed in the form

$$\hat{U}(t) = e^{-i/\hbar g_1(t)\hat{J}_x} e^{-i/\hbar g_2(t)\hat{J}_y} e^{-i/\hbar g_3(t)\hat{J}_z} e^{-i/\hbar g_4(t)} . \quad (12)$$

If this is the case, substitution of (12) into (10) gives rise to differential equations for $g_i(t)$ in terms of the (known) potentials $V_i(t)$. Once $\hat{U}(t_1, t)$ is known, the scattering matrix is defined in terms of it as

$$\hat{S} = \hat{U}(-\infty, \infty) , \quad (13)$$

i.e., the transition probabilities can be obtained through

$$\begin{aligned} P(|jm\rangle \rightarrow |jm'\rangle) &= |\langle jm|\hat{S}|jm'\rangle|^2 \\ &= \left| \sum_{\tau m_2} e^{-i\beta_1 \tau} d_{\tau m'}^j(-\pi/2) d_{\tau m_2}^j(-\pi/2) d_{m_2 m}^j(\beta_2) \right|^2 , \end{aligned} \quad (14)$$

where $\beta_i = g_i(-\infty, \infty)/\hbar$ and the d-functions are the usual Jacobi functions appearing in the definition of Wigner's D-functions [8].

3 Calculations

The main stumbling block for the evaluation of the evolution operator is the calculation of $\hat{V}_{int}(t)$ through (11). We proceed to discuss briefly some approximations to carry out this task.

a) Sudden Approximation

In the sudden approximation, the interaction time is considered to be very short. A Taylor expansion of (11) along t_1 leads to

$$\hat{V}_{int}(t) = V(t) + \frac{i}{\hbar}[\hat{H}_0, V(t)]V(t - t_1) + \dots \quad (15)$$

which at zeroth order gives $\hat{V}_{int}(t) = V(t)$. This represents an approximation where all dynamical information of the molecular potential is lost in equation (10). We may then solve for the classical trajectories using (12), in some cases analytically, which generalize results known previously for the exponential interaction (6d) [9]. In this limit we are able to exactly reproduce the analysis of Levine and Wulfman [10,11] and extend them to the more general interactions in (6). We omit these results here for lack of space and refer the reader to reference [9].

b) Averaging Techniques for $\hat{V}_{int}(t)$

Since we are interested in comparing our algebraic methods with quantum mechanical *ab initio* calculations (when these are available), we should improve the evaluation of \hat{V}_{int} so as to introduce the dynamical effects of the molecular potential. The sudden approximation of the previous subsection fails to account for the fine properties required. Fortunately, a quantum mechanical calculation for the transition probabilities in the scattering of an atom from a one-dimensional Morse oscillator has been presented by Clark and Dickinson [12], so we may gauge our approximations by comparing with their results. Returning to eq. (11), we substitute (6a) and make use of the commutation relations

$$\begin{aligned} [J_z^2, \hat{J}_y] &= -\hat{J}_y - 2i\hat{J}_z\hat{J}_x \quad , \\ [J_z^2, \hat{J}_x] &= -\hat{J}_x + 2i\hat{J}_z\hat{J}_y \quad . \end{aligned} \quad (16)$$

After some algebra we find the expression

$$\begin{aligned} \hat{V}_{int}(t) &= \left[\frac{-i}{2\sin(x_0\omega_0 t)} \left(-\cos(2x_0\omega_0 t\hat{J}_z)\hat{J}_y + \hat{J}_y \cos(2x_0\omega_0 t\hat{J}_z) \right) \right. \\ &+ \left. \frac{1}{2\sin(x_0\omega_0 t)} \left(-\cos(2x_0\omega_0 t\hat{J}_z)\hat{J}_y + \hat{J}_y \cos(2x_0\omega_0 t\hat{J}_z) \right) \right] V_3(t) \\ &+ V_1(t)\hat{J}_{z_1} + V_2(t) \quad , \end{aligned} \quad (17)$$

where $x_0\omega_0$ is the standard anharmonicity parameter, which can be expressed in terms of the Morse potential parameter through $x_0\omega_0 = \frac{-A}{\hbar}$. The problem with eq. (17) is that it no longer satisfies being linear in the $SU(2)$ generators, so (12) is not valid. To deal with this problem, we proceed as follows. We apply $\hat{V}_{int}(t)$ to a Morse eigenfunction $|jm\rangle$ and insert a complete set of states $\sum_{\mu} |j\mu\rangle\langle j\mu|$ to the resulting expression. Taking into account the selection rules for \hat{J}_y , which imply, $\mu = m \pm 1$, we find a state-dependent potential:

$$\begin{aligned} \hat{V}_m(t) &= \left(\frac{\cos(2x_0\omega_0 tm)}{\cos(x_0\omega_0 t)} V_3(t) + \frac{\cos(2x_0\omega_0 t(m+1))}{\cos(x_0\omega_0 t)} V_3(t) |jm+1\rangle\langle jm+1| \right. \\ &+ \left. \frac{\cos(2x_0\omega_0 t(m-1))}{\cos(x_0\omega_0 t)} V_3(t) |jm-1\rangle\langle jm-1| \right) \hat{J}_y + V_1(t)\hat{J}_z + V_2(t) \quad . \end{aligned} \quad (18)$$

The m -dependent cosine functions, however, are practically the same for small values of the phonon number $v = j - m$ (large m values), so we can simplify (18) by averaging the excitation to the two possible states $\mu = m \pm 1$, so we arrive at the simple m -dependent potential

$$\begin{aligned} \hat{V}_m(t) = & (\cos(2x_0\omega_0tm) \cos(x_0\omega_0t)V_3(t)\hat{J}_y \\ & + V_1(t)\hat{J}_z + V_2(t) \ , \end{aligned} \quad (19)$$

which is linear in the $SU(2)$ generators, so (12) is valid. Since we are interested in comparing our approach with the calculations of ref. [12] where only $V_3(t) \neq 0$, the potential (19) simplifies further and only \hat{J}_y remains. The evolution operator is then given by

$$\hat{U}_m(t) = e^{-ig_2(m,t)\hat{J}_y/\hbar} \ , \quad (20)$$

where

$$g_2(m, t) = V_3 \cos(x_0\omega_0t) \cos(2x_0\omega_0mt) \ . \quad (21)$$

The differential equation for the evolution operator then lead to exactly solvable forms for the classical trajectories and to the asymptotic value of $g_2(m, t)$ (see below (14))

$$\beta_2(m) = \frac{E}{\hbar} \int_{-\infty}^{\infty} \cos(x_0\omega_0t) \cos(2mx_0\omega_0t) \operatorname{sech}^2 \left(\sqrt{\frac{E}{2\mu}} \frac{t}{a_0} \right) dt \quad (22)$$

where E is the collision energy. From (14) this leads to the simple expression for the transition probabilities

$$P(|jm \rangle \rightarrow |jm' \rangle) = d_{m,m'}^j(\beta_2(m')) \ , \quad (23)$$

where

$$\beta_2(m') = \frac{\mu\omega_0\pi a_0^2}{b^2\hbar} \left[\frac{(2m' - 1)x_0}{\sinh((2m' - 1)x_0k_0)} + \frac{(2m' + 1)x_0}{\sinh((2m' + 1)x_0k_0)} \right] \ , \quad (24)$$

with $k_0 = \frac{\omega_0 a_0 \pi}{b} \sqrt{\frac{\mu}{2E}}$. In Table I we compare the results of our calculation, using (23), (24), with those of Clark and

TABLE I. Comparison between the algebraic model and the Clark-Dickinson Model¹²⁾

Energy ($\hbar\omega_0 / 2$ units): 16

Final state	Initial State = 0		Initial State = 1	
	Clark-Dickinson Probability	Model Probability	Clark-Dickinson Probability	Model Probability
1	0.245000	0.157837		
2	3.38000E(-02)	1.45652E(-02)	0.318000	0.253196
3	2.72000E(-03)	8.65153E(-04)	5.72000E(-02)	3.62444E(-02)
4	1.61000E(-04)	3.71652E(-05)	5.16000E(-03)	2.86219E(-03)

5 7.44000E(-06) 1.22993E(-06) 3.24000E(-04) 1.50963E(-04)

Energy ($\hbar\omega_0/2$ units): 12

	Initial State = 0		Initial State = 1	
Final state	Clark-Dickinson Probability	Model Probability	Clark-Dickinson Probability	Model Probability
1	0.129000	0.124019		
2	6.65000E(-03)	8.57432E(-03)	0.167000	0.208828
3	1.49000E(-04)	3.81572E(-04)	8.41000E(-03)	2.19917E(-02)
4	1.48000E(-06)	1.22807E(-05)	1.38000E(-04)	1.28983E(-03)
5	4.95000E(-09)	3.04486E(-07)	7.01000E(-07)	5.07090E(-05)

Energy ($\hbar\omega_0/2$ units): 10

	Initial State = 0		Initial State = 1	
1	7.39000E(-02)	0.105782		
2	1.66000E(-03)	6.09133E(-03)	8.15000E(-02)	0.182403
3	1.17000E(-05)	2.25776E(-04)	1.22000E(-03)	1.58582E(-02)
4	1.95000E(-08)	6.05219E(-06)	5.12000E(-06)	7.71373E(-04)
5	0.	1.24982E(-07)	2.95000E(-10)	2.51949E(-05)

Energy ($\hbar\omega_0/2$ units): 8

	Initial State = 0		Initial State = 1	
1	3.15000E(-02)	8.66178E(-02)		
2	1.85000E(-04)	3.98810E(-03)	2.28000E(-02)	0.152903
3	1.18000E(-07)	1.18193E(-04)	3.07000E(-05)	1.05375E(-02)
4	0.	2.53330E(-06)	1.37000E(-11)	4.08112E(-04)
5	0.	4.18294E(-08)	0.	1.06318E(-05)

Energy ($\hbar\omega_0/2$ units): 6

	Initial State = 0		Initial State = 1	
1	7.31000E(-03)	6.64920E(-02)		
2	2.30000E(-06)	2.29488E(-03)	1.25000E(-03)	0.120126
3	0.	5.09821E(-05)	0.	6.15327E(-03)
4	0.	8.19113E(-07)	0.	1.77900E(-04)

5

0.

1.01384E(-08)

0.

3.46550E(-06)

Dickinson [12] for different collision energies and for two different initial states. Although our results differ from the exact ones, particularly for higher final states where the probabilities are very small, the general trend is reproduced remarkably well, taking into account our semiclassical method.

4 Conclusions

The algebraic model seems to provide an attractive alternative to integro-differential techniques for the description of atom-molecule collisions. The approximation methods developed for the one-dimensional test model can be readily extended to the three dimensional case and applied to real systems [2,3]. We are currently exploring the generalization of these techniques to include reaction channels, which would represent an important development because of the relevance of these processes in atmospheric interactions [13].

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References

- [1] J. Récamier, D. Micha, B. Gazdy, *J. Chem. Phys.* **85**, 5093 (1986); J. Récamier and J. Ortega, *Mol. Phys.* **73**, 635 (1991); H. K. Shin, *J. Phys. Chem.* **77**, 2657 (1973); T. Ree, Y. H. Kim and H. K. Shin, *Chem. Phys. Lett.* **103**, 149 (1983); B. Gazdy and D.A. Micha, *J. Chem. Phys.* **82**, 4926 (1985).
- [2] L. Goubert, G. D. Billing, E. Desoppere and W. Wieme, *Chem. Phys. Lett.* **219**, 360 (1994) and references therein.
- [3] S. K. Pogrebnya and D. C. Clary, *Chem. Phys. Lett.* **219**, 366 (1994) and references therein.
- [4] F. Iachello, *Chem. Phys. Lett.* **78**, 581 (1981).
- [5] A. Frank, R. Lemus, J. Récamier and A. Amaya, *Chem. Phys. Lett.* **193**, 176 (1992).
- [6] A. Frank and P. Van Isacker, *Algebraic Methods in Molecular and Nuclear Structure Physics*, Wiley, New York, (1994).
- [7] O. S. van Roosmalen, Ph. D. Thesis, University of Groningen, The Netherlands (1982).
- [8] M. E. Rose, *Elementary Theory of Angular Momentum*, Wiley, New York, (1969).
- [9] R. D. Santiago, A. Frank and R. Lemus, *J. Chem. Phys.* to be published.

- [10] K. Wulfman and R. D. Levine, *Chem. Phys. Lett.* **97**, 361 (1983).
- [11] R. D. Santiago, A. Frank and R. Lemus, *Chem. Phys. Lett.*, to be published.
- [12] A. P. Clark and A. S. Dickinson, *J. Phys. B: Atom. Molec. Phys.* **16**, 164 (1973).
- [13] M. J. D'Mello, D. E. Manolopoulos and R. E. Wyatt, *Science* **263**, 102 (1994).